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THERMAL SAFETY CHARACTERIZATION AND EXPLOSION VIOLENCE OF ENERGETIC MATERIALS

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Thermal safety characterization and explosion violence of energetic materials

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Abstract. Some explosives could thermally explode at fairly low temperatures and the violence from thermal explosion may cause significant damage. Thus it is important to understand the response of energetic materials to thermal insults. The One Dimensional Time to Explosion (ODTX) system at the Lawrence Livermore National Laboratory has been used since 1970 to measure times to explosion, threshold temperature for thermal explosion, and determine kinetic parameters of energetic materials. The ODTX testing can also provide useful data for assessing the thermal explosion violence of energetic materials. Recent ODTX experimental data on LLM-105, RX-55-DQ, and LLM-191 are reported in the paper. The new capabilities developed for the ODTX system are also briefly described.

1. Introduction

Thermal explosion due to fires and other insults would cause significant damage to structures and loss of life. There has been an extensive study on the thermal decomposition and thermal explosion of energetic materials at elevated temperatures in different confinements and sample geometries (one-dimensional and two-dimensional) [2,3,4]. Examples are STEX (scaled-thermal-explosion-experiment) system[5] at LLNL and SITI (Sandia-instrumented-thermal-ignition) system at SNL[6]. The ODTX system at the Lawrence Livermore National Laboratory (LLNL) has been used for decades for cook-off study[7-11]. The ODTX testing generates the following technical data: (1) lowest temperature at which thermal explosion would occur (threshold temperature, T_{li}); (2) times to thermal explosion at temperatures above T_{li} for the calculation of activation energy and frequency factor; and (3) thermal explosion violence. It is a useful tool that is being used routinely at LLNL for the characterization of new energetic materials at LLNL.

2. System Description and Experiments

Energetic materials in various sample configurations can be tested in the ODTX system. An aluminum shell is used to hold powder samples, pasty samples, or liquid samples. Pressed and cast samples are delivered to the cavity of aluminum anvils directly without the use of the aluminum shell. The testing involves heating a 1.27-cm diameter spherical sample in a spherical cavity between two aluminum anvils. The sample is remotely delivered to the anvil cavity via the sample delivery system when the anvils reach a predetermined temperature. A microphone sensor measures a sound signal, which indicates the time at which a thermal explosion occurs. The detail description of the LLNL ODTX system can be found elsewhere [1].

3. Recent Experimental Results

3.1 Small-scale safety test results on LLM-105 and LLM-191

LLM-105 (2,6-diamino-3,5-dintropyrazine-1-oxide) is a potential insensitive high explosive under development at LLNL. LLM-105 is attractive for its high density and good performance[12]. LLM-191 (3,5-bis(nitro-1,25,-oxadiazol)-1,2,4-oxidaizolel) has very low melting point (61 C) and high density (TMD = 1.90 g/cc), is a candidate ingredient for melt casted propellant formulations. Table 1 lists the small-scale safety test data and performance data. Both materials are insensitive to impact, friction, spark, thermally stable at 120 C and with DSC peak exotherms 361 °C and 295 °C, respectively. With high detonation velocity and CJ pressure, they may find applications in weapon systems in the future.

Table 1. Small-scale safety and performance test results for LLM-105 and LLM-191

Tests	**LLM-105**	**RX-55-DQ (94% LLM-105, 6% binder)**	**LLM-191**
Impact sensitivity (drop hammer), cm	91	141	114
Friction sensitivity, kg	0/10 @ 36.0 kg	0/10 @ 36.0 kg	1/10 @ 15.2 kg
Spark sensitivity	0/10 @ 1.0 J @ 510 Ohms	0/10 @ 1.0 J @ 510 Ohms	0/10 @ 1.0 J @ 510 Ohms
Chemical Reactivity (CRT) at 120 °C	0.20 cc/g	0.01 cc/g	0.34 cc/g
DSC	Peak temperature at 361 °C	Peak temperature at 359 °C	Peak temperature at 295 °C
Density, g/cc	1.918	1.909	1.900
Detonation velocity*, km/s	N/M	7.8	8.6
P_{CJ}, GPa*	N/M	27	35

- Measured at pressed density of 1.8 g/cc

3.2 ODTX times to explosion data for LLM-105 and RX-55-DQ

RX-55-DQ (a LLM-105 formulation) was pressed into 0.5 inch spherical parts and were tested in the ODTX system over a range of temperature. Totally 10 ODTX shots were performed on RX-55-DQ. The times to thermal explosion data are shown in table 2 and table 3 for RX-55-DQ and LLM-105, respectively. The test data are plotted in figure 1. The figure also shows ODTX data for neat LLM-105 with different density. Without binder, neat LLM-105 was difficult to form pressed parts of high density. Most of the ODTX shots on neat LLM-105 were conducted with LLM-105 powder with a packed density of 59% TMD. The times to explosion for packed powder were longer than that of pressed part (83% TMD) due to slower heat transfer, higher voids, and less material. ODTX data for PETN, RDX, HMX, and TATB are also shown for comparison. The ODTX test results indicated that the thermal sensitivity of RX-55-DQ was between those of TATB and HMX. Reproducibility was good. Testing was repeated at 241.7 °C twice and times to explosion were fairly close.

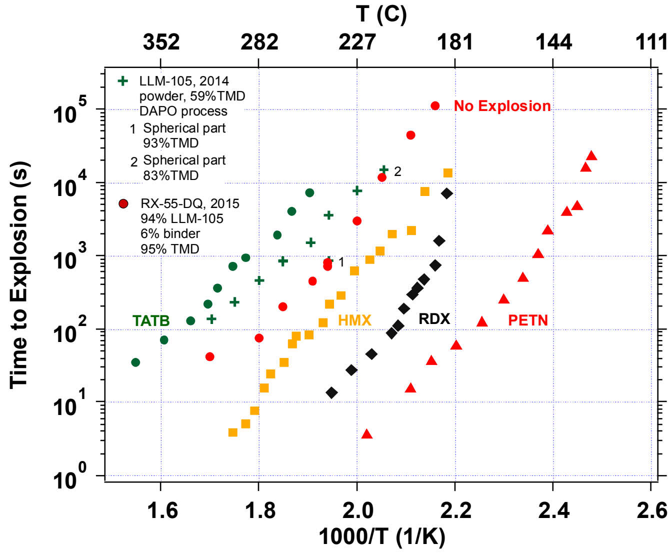

Figure 1. ODTX results of RX-55-DQ and neat LLM-105.

Table 2. Times to thermal explosion data for RX-55-DQ

Test #	Temp., ºC	Temp., 1000/K	Time to Explosion, second	Note
1	314.1	1.70	41.9	
2	282.4	1.80	76.9	
3	267.4	1.85	205	
4	251.6	1.91	450	
5	241.7	1.94	724	
6	241.7	1.94	806	Repeated
7	226.9	2.00	3,052	
8	213.7	2.05	11,908	
9	201.8	2.11	45,275	
10	190.5	2.16	113,232 (31.5 hours)	No thermal explosion (NO-GO)

Table 3. Times to thermal explosion data for neat LLM-105 packed powder (59% TMD) and pressed parts

Test #	Temp., ºC	Temp., 1000/K	Time to Explosion, second	Note
1	314.1	1.70	139.6	Packed powder
2	298.3	1.75	235.9	Packed powder
3	282.4	1.80	471.8	Packed powder
4	267.4	1.85	851.4	Packed powder
5	267.4	1.85	863	Repeated, packed powder
6	251.6	1.91	1547.1	Packed powder
7	241.7	1.94	869.9	Packed powder
8	241.7	1.94	3638.5	83% TMD pressed part
9	226.9	2.00	7811.6	Packed powder
10	213.7	2.05	14,931	93% TMD pressed

				part

3.3 ODTX times to explosion data for LLM-191

Neat LLM-191 powder was pressed into 0.5 inch spherical parts at low temperature. These parts were tested in the ODTX system over a range of temperature. The times to thermal explosion data are shown in Figure 2 and Table 4. ODTX data for PETN, RDX, HMX, and TATB are also shown for comparison. The results indicated that the thermal sensitivity of LLM-191 was similar to another commonly used casted explosive TNT at high temperature region. At lower temperature region (< 230 °C), its thermal sensitivity is close to that of TATB, thus LLM-191 and TATB have similar threshold temperature for thermal explosion.

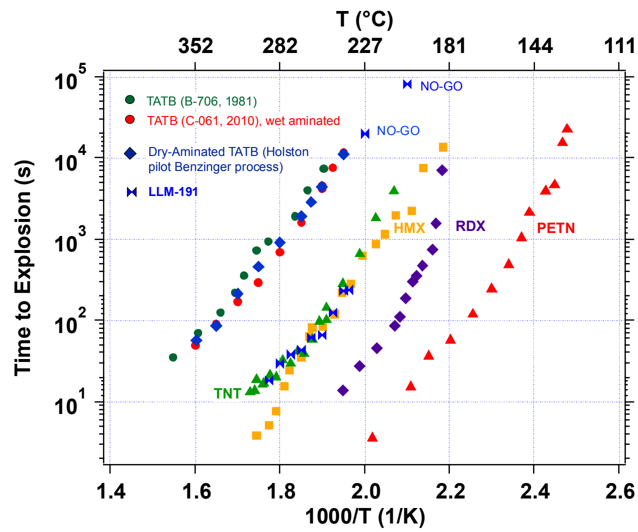

Figure 2. ODTX results of neat LLM-191.

Table 4. Times to thermal explosion data for LLM-191

Test #	Temp., °C	Temp., 1000/K	Time to Explosion, second	Note
1	290.2	1.78	18.4	
2	282.4	1.80	29.5	
3	274.8	1.83	38.1	
4	267.4	1.85	43.8	
5	260.2	1.88	62.6	
6	253.2	1.90	67.3	
7	246.3	1.93	126.3	
8	239.7	1.95	233.2	
9	236.4	1.96	239.7	
10	226.9	2.00	20,220 (5.6 hours)	No thermal explosion (NO-GO)
11	203.0	2.10	81,743 (22.7 hours)	No thermal explosion (NO-GO)

3.4. Threshold temperature for thermal explosion (T_{lj})

Table 5 shows the lowest temperatures at which thermal explosion (threshold temperature, T_{li}) would occur. ODTX testing on RX-55-DQ at 190.5 ^{o}C showed no thermal explosion occurred after 31.5 hours. The threshold temperature for LLM-191 is 227 ^{o}C that is much higher than that of TNT although both have fairly low melting points.

Table 5. Threshold temperature, T_{li}

Materials	**T_{li}, ^{o}C**
PETN	120
RDX	175
HMX	180
LLM-105	NT
RX-55-DQ	190
TNT	200
LLM-191	227
TATB	230

NT- not tested

3.5. Thermal explosion violence

Figure 3 shows the anvils before and after the thermal explosion of LLM-191. The anvils indicated some melting from the extremely hot gas generated by the explosion. The blast energy (energy of explosion) from the thermal explosion can be estimated from the crater size in the aluminum anvils [3, 11]. A surface profilometer was used to measure the increase in crater volume after the blast. The anvils indicated some melting from the extremely hot gas generated by the thermal explosion. A detailed description and comparison of thermal explosion violence for various energetic material was previously reported by Hsu et. al[9]. Figure 4 shows the anvils after thermal explosion, indicates the explosion violence for LLM-105 formulation (RX-55-DQ) and LLM-191 is lower than that for PBX-9501.

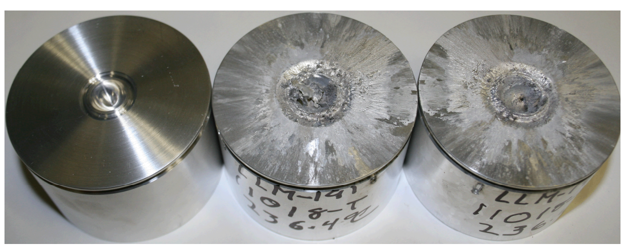

Figure 3. Anvils before and after thermal explosion of LLM-191 at 236.4 °C; left was the pristine anvil; also shown are top anvil (middle) and bottom anvil (right) after the thermal explosion.

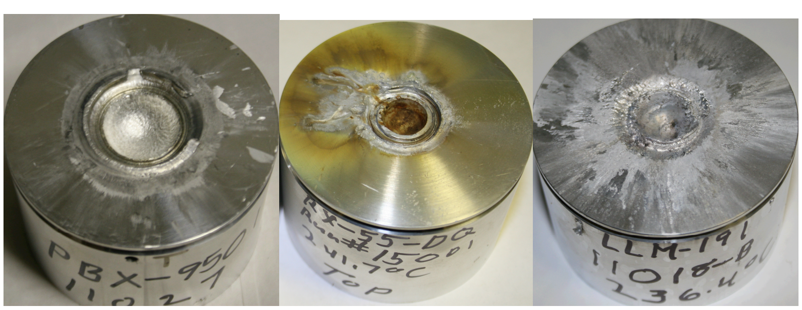

Figure 4. Anvil after thermal explosion; left for PBX-9501, middle for RX-55-DQ, right for LLM-191

4. **Pressure Measurement- A New Diagnostics of the ODTX System (P-ODTX)**

Gas pressure of energetic materials in confinement at high temperatures is important to understand the thermal decomposition kinetics of energetic materials. The pressure data also offers the opportunity to validate the existing cook-off models in the ALE3D code and helps to determine whether weapon system cases or improvised devices would burst when they are under thermal insults (to avoid further structure damage and casualty) before thermal explosion would occur. We recently conducted experiments to measure decomposition gas pressure for LX-10 at 170 °C and the results are shown in Figure 5. The pressure data will be used to validate the cook off models in the ALE3D code.

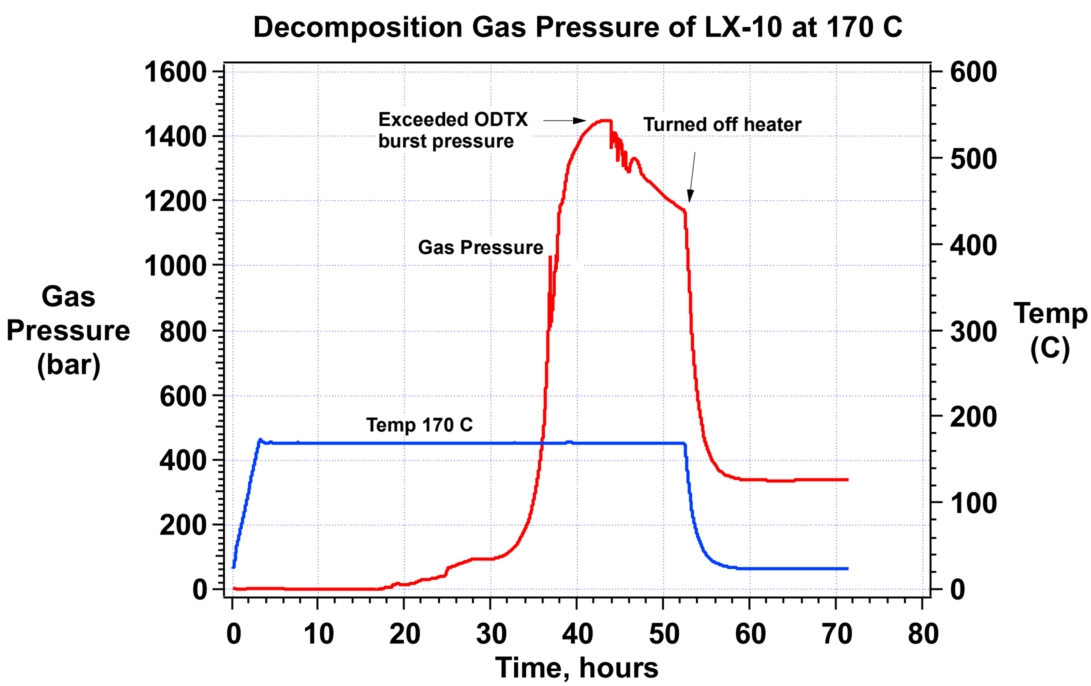

Figure 5. Gas pressure of LX-10 at 170 °C

5. **Gas Composition Measurement (C-ODTX)- A New Diagnostics Under Development**

Gas composition data for explosive under thermal insults are crucial for gas pressure prediction and cook-off modeling. The technique is under development. We will use NIR spectroscopy to characterize evolved gases during an ODTX experiment in elevated temperature and high pressure. Fiber optics will be used to transmit and receive light to/from the ODTX cavity. We are testing the survivability of fiber optics at high temperature and high pressure (external to the ODTX system), see figure 6.

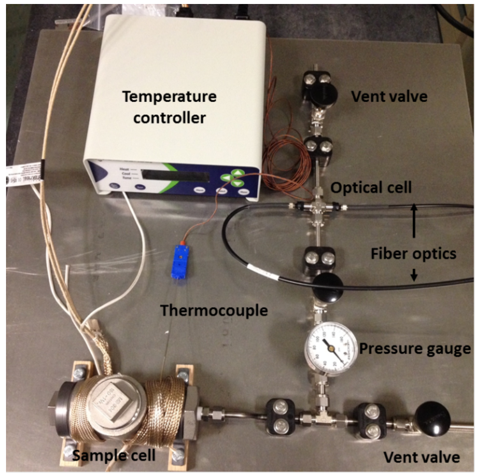

Figure 6. Fiber optic test assembly

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